



Workshop

**Jordan University of Science and
Technology**

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Chemical Management Best Practices / Pesticide Management

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Environmental & Chemical Safety Educational Institute



Chemical Management



Best Practices



References

“Less is Better,” American Chemical Society, Washington DC, 2003, available online:

<http://membership.acs.org/c/ccs/publications.htm>



“School Chemistry Laboratory Safety Guide,” US NIOSH Publication 2007-107, Cincinnati, OH, 2006, available on-line:

<http://www.cpsc.gov/CPSCPUB/PUBS/NIOSH2007107.pdf>

“Prudent Practices in the Laboratory: Handling and Disposal of Chemicals,” National Academy Press, 1995, available online:

http://www.nap.edu/catalog.php?record_id=4911



Chemical Management

Institute a Safety Program

- Have a Safety Manual
- Appoint a chemical safety officer for each major area/section/group/building
- Form a Safety Committee
- Have periodic safety training (films, etc)
- Have safety inspections
- Investigate serious accidents/incidents
- Follow-up!

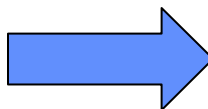




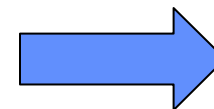
Cradle - to - grave care of chemicals



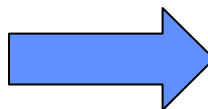
Receipt



Storage



Use



Disposal

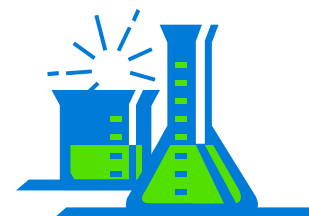




Plan experiments in advance!

What chemicals are needed?

How much is needed?



How will the chemicals be handled?

What are the reaction products?

How will the chemical be stored?

How will disposal take place?





Inventory management

Less is Better !

- Order only what you need
- Reduce size of experiment
 - It costs less to store
 - It costs less to dispose

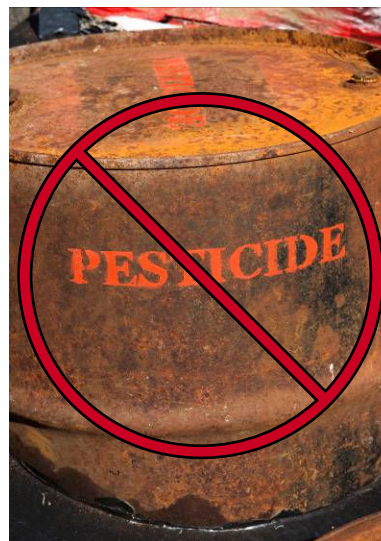


“Less is Better: Guide to minimizing waste in laboratories”, Task Force on Laboratory Environment, Health and Safety, American Chemical Society, 2002. http://membership.acs.org/C/CCS/pub_9.htm



Inventory management

- How old are your chemicals?
- Some chemicals degrade over time
 - rotate stock
 - label & date





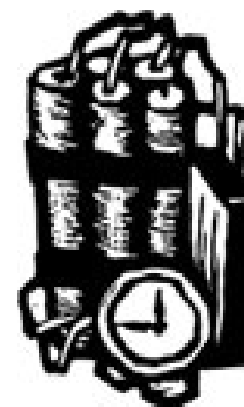
Inventory management



Less is Better !
It's Safer!

It may be cheaper to order **diethyl ether** in large containers

But, if it's opened for a long time—peroxides can form!





Inventory management

-R-O-O-R-

Peroxide Forming Chemicals

Even with inhibitors they can become dangerous over time

Examples: ethers, dioxane, tetrahydrofuran

- discard or test if unsure
 - label & date when received, when opened, and provide expiration date

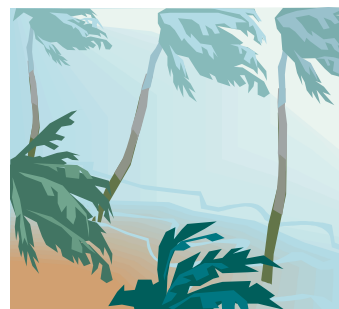
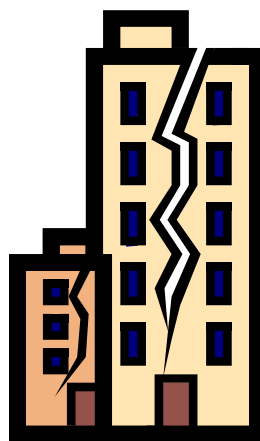
References: See for example, http://www.med.cornell.edu/ehs/updates/peroxide_formers.htm





Chemical storage

- Protect chemicals during normal operations
- Protect chemicals during unexpected events
 - Floods
 - Tidal waves
 - Earthquakes
 - Typhoons
 - Hurricanes





Chemical storage: Basic concepts

- **Separate incompatible chemicals**
- **Separate flammables/explosives from ignition sources**
- **Use flammable storage cabinets for large quantities of flammable solvents**
- **Separate alkali metals from water**
- **Separate acids and bases**





Use flammables storage cabinets





Chemical storage: Basic concepts

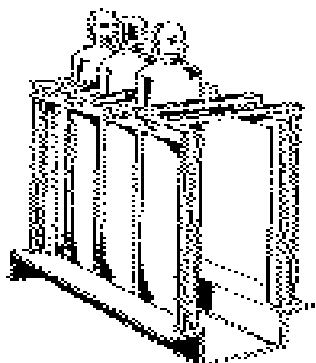
- Store nitric acid separately
- Store large containers on bottom shelves
- Lock up drugs, chemical surety agents, highly toxic chemicals
- Do not store food in refrigerators with chemicals





Chemical storage: Gas cylinders

- **Secure (chain/clamp) and separate gas cylinders**
 - **Screw down cylinder caps**
 - **Store in well-ventilated area**
 - **Separate & label empty cylinders**
 - **Store empty cylinders separately**
- **Separate flammable from reactive/oxidizing gases**





Improper gas cylinder storage





Gas Cylinders



Exploded nitrogen cylinder





Chemical storage: Cryogenics

- **Store gases & cryogenics separately from other chemicals**
- **Store cryogenics (liquid nitrogen) & dry ice in well ventilated areas**
- **Use proper PPE (including eye protection) when handling & moving cryogenics**
- **Do not use cryogenics in closed areas**





Chemical storage: Good practices

- **Limit access**
 - Label “Authorized Personnel Only”
 - Lock area/room/cabinets when not in use
- **Be sure area is cool and well ventilated**
- **Secure storage shelves to wall or floor**
- **Shelves should have a $\frac{3}{4}$ ” front lip**
 - In earthquake territory, have a rod several inches above shelf
- **Separate incompatible chemicals**
 - Organize chemicals by compatible groups
 - Alphabetize chemicals only within compatible groups





Chemical storage: Bad practices

- **Do Not Store Chemicals**

- on top of cabinets
- on floor
- in hoods
- with food or drinks
- in refrigerators used for food
- where there are wide variations in temperature, humidity or sunlight





Chemical storage: Containers

- Don't use chemical containers for food
- Don't use food containers for chemicals
- Be sure all containers are properly closed
- Wipe-off outside of container before returning to storage area
- Transport/carry all containers safely
 - Preferably use outer protective container





Improper chemical storage



**Never use hallways
for storage**

Safety Hazard!!

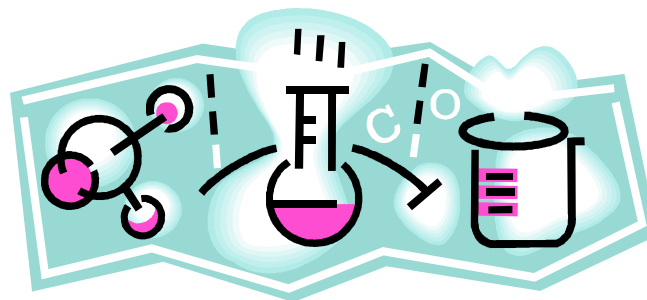
**Blocks exit path in
emergencies!!!**



Suggested shelf storage groups: Organics

- Acids, anhydrides
- Alcohols, amides, amines
- Aldehydes, esters, hydrocarbons
- Ethers, ketones, halogenated hydrocarbons
- Epoxies, isocyanates
- Azides, peroxides
- Nitriles, sulfides, sulfoxides
- Cresols, phenols

From: "School Chemistry Laboratory Safety Guide," US NIOSH Publication 2007-107





Suggested shelf storage groups: Inorganics

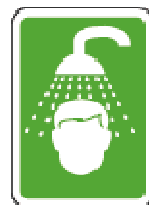
- Metals, hydrides
- Halides, halogens, phosphates, sulfates, sulfides
- Amides, azides, nitrates, nitrites
- Carbonates, hydroxides, oxides, silicates
- Chlorates, chlorites, perchlorates, peroxides
- Arsenates, cyanides, cyanates
- Borates, chromates, manganates
- Acids
- Arsenics, phosphorus, sulfur

From: "School Chemistry Laboratory Safety Guide," US NIOSH Publication 2007-107



Waste management: General guidelines

- Secure and lock waste storage area
- Post signs to warn others
- Keep area well ventilated
- Provide fire extinguishers and alarms, spill kits
- Provide suitable PPE
- Provide eye wash, safety showers
- Do not work alone





Waste management: General guidelines

- Insure against leakage; dyke area if possible
- Label all chemicals, containers, vials
- Separate incompatible chemicals
- Keep gas cylinders separate
- Keep radioactive material separate
- Know how long waste can be stored
- Provide for timely pick-up



Dangerous waste management





Waste management

- **Recycle, reuse, redistill if possible**
- **Dispose by incineration, if possible**
- **Incineration is NOT the same as open burning**

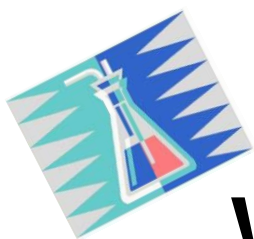




Waste management: Waste disposal service

- Is disposal service licensed?
- How will waste be transported?
- How will waste be packaged?
- Where will material be disposed?
- How will it be disposed?
- Maintain written records

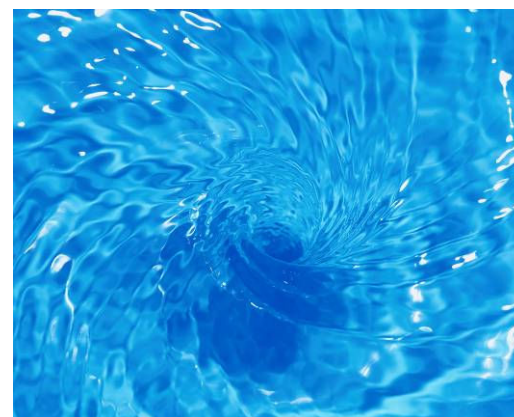




Waste management: Down the drain?

If legally allowed:

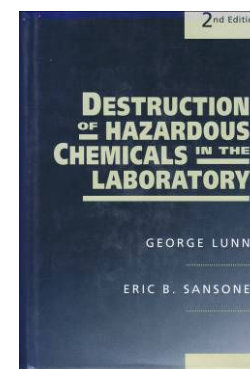
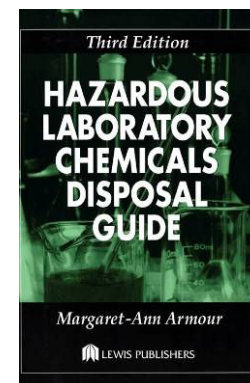
- **Deactivate & neutralize some liquid wastes yourself**
 - e.g., acids & bases
 - Don't corrode drain pipes
- **Dilute with lots of water while pouring down the drain**
- **Be sure that you do not form more hazardous substances**





Waste management: Treatment in Lab?

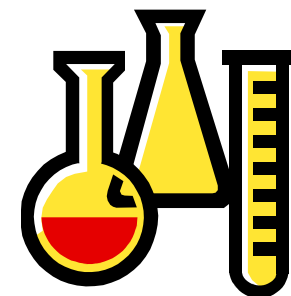
- Destruction / neutralization of hazardous chemicals
 - May or may not be allowed by regulations
 - Must be done by trained chemist
 - Specific to each chemical
- References:
 - “Procedures for the Laboratory-Scale Treatment of Surplus and Waste Chemicals, Section 7.D in Prudent Practices in the Laboratory: Handling and Disposal of Chemicals,” National Academy Press, 1995, available online: http://www.nap.edu/catalog.php?record_id=4911
 - “Destruction of Hazardous Chemicals in the Laboratory, 2nd Edition”, George Lunn and Eric. B. Sansone, Wiley Interscience, 1994, ISBN 978-0471573999.
 - “Hazardous Laboratory Chemicals Disposal Guide, Third Edition”, Margaret-Ann Armour, CRC Press, ISBN 978-1566705677





Chemical management

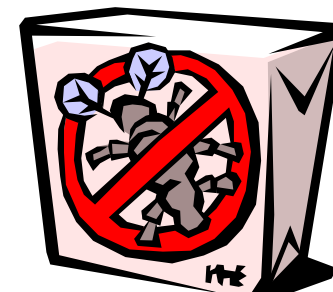
- Proper chemical management is an important part of laboratory safety and security
- Helps protect people, laboratories and the environment
- Can save money by avoiding duplicate chemical purchases





History of Pesticides

- The first pesticides developed 4500 years ago: crop dusting with elemental sulfur.
- Modern pesticides
 - Main development/discovery period, 1870's to 1945.
 - DDT first synthesized in 1874, used as a pesticide in 1939, became the most widely used pesticide in the world.
 - Advances in organic chemistry and chemical engineering lead to mass production, especially after WWII.
- Uses
 - Health-Medical
 - Delousing, fumigation, precursors for pharmaceutical drugs.
 - Indoor spraying with DDT for malaria control recommended by WHO.
 - Used to prevent the spread of malaria, bubonic plague, sleeping sickness and typhus.
 - Agriculture
 - Pest control to prevent crop losses.
 - Financial advantage for farmers.



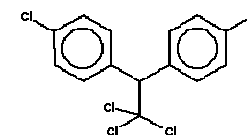


Main pesticide categories

- **Organochlorines:**

- **Chlordane**, **DDT**, **Dieldrin**, 2,4,5-T, Lindane, **Heptachlor**, Pentachlorophenol, **Endrin**, **Aldrin**, Chlordecone, Endosulfan, **Hexachlorobenzene**, Methoxychlor, **Mirex**, **Toxaphene**, TDE.

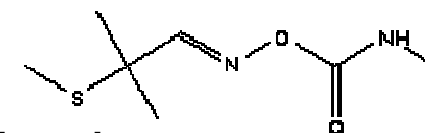
- Chemical warfare agents: sulfur mustard, HD.



- **Organophosphates:**

- Esters of phosphoric acid, Parathion, Malathion, Methyl Parathion, Chlorpyrifos, Diazanone, Dichlorvos, Phosmet, Tetrachlorvinphos, Azinphos Methyl, Naled, Fenthion, Dimethoate, Acephate, phosalone and others.

- Chemical warfare agents: sarin, tabun, soman and VX.



- **Carbamates:**

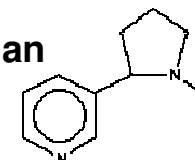
- Carbaryl, Sevin, Aldicarb, Carbofuran, Furadan, Fenothiocarb

- **Pyrethroids:**

- Synthetic chemical compound similar to natural pyrethrins produced by the flowers of pyrethums (*Chrysanthemum cinerariaefolium* and *C. coccineum*).
- Common in household insecticides and insect repellent. At concentrations used in such products, they are generally harmless to human beings, except sensitive individuals.

- **Neo-nicotinoids:**

- Synthetic analogs of nicotine insecticides, exhibit much lower mammalian toxicity and greater field persistence.
- Used in place of organophosphates and carbamates



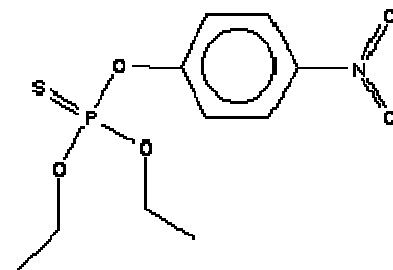
Red: banned by Stockholm Convention



Pesticides categorized by toxicity

Class		LD50 for the rat (mg/kg body weight)			
		Oral		Dermal	
		Solids	Liquids	Solids	Liquids
Ia	Extremely hazardous	5	20	10	40
Ib	Highly hazardous	5 - 50	20 - 200	10-100	40 – 400
II	Moderately hazardous	50 - 500	200 - 2000	100-1000	400 – 4000
III	Slightly hazardous	Over 500	Over 2000	Over 1000	Over 4000

- Class Ia: Aldicarb, Hexachlorobenzene, Parathion
- Class Ib: Carbofuran, Dichlorvos, Nicotine
- Class II: Chlordane, Carbaryl, Chlorpyrifos, DDT, Naled
- Class III: Acephate, Fenothiocarb, Malathion



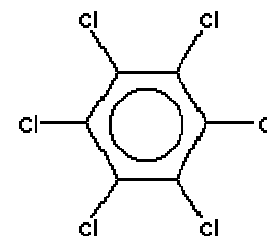
“The WHO Recommended Classification of Pesticides by Hazard and Guidelines to Classification, 2004”, updated June 2006, http://www.who.int/ipcs/publications/pesticides_hazard_rev_3.pdf



Bad effects/properties of pesticides

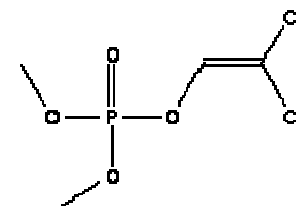
- **Organochlorines**

- Accumulates in human adipose tissue and human breast milk
- Accumulates and persists in animal milk and dairy products
- Interferes with estrogen and androgen receptors
- Suppresses immune system
- Targets sodium ion channels making powerful convulsants
- Can induce neurobehavioral problems
- Can cause cancer, possibly including breast cancer
- Long term exposure linked to type 2 diabetes
- Extremely long half life remaining ecologically active for years-to-decades once applied in the environment.



- **Organophosphates,**

- Acts against the enzyme acetylcholinesterase or cholinesterase by irreversibly inactivating it.
- Degrades much more quickly in the environment than organochlorines
- Organophosphates are generally more toxic than organochlorines.
- Most common source of poisoning world-wide.
- Intentionally used for suicides in agricultural areas.
- Closely related to chemical warfare 'nerve' agents (sarin, tabun, soman and VX).





Problems with pesticide use

- **Persistence**

- Organochlorine pesticides resist degradation. Half-lives range from months to years to decades.
- Organophosphates are less persistent in the environment, but tend to be more toxic to other species (including humans and warm-blooded animals).
- Pesticides are found in surface and ground-waters, agricultural fields and farms, urban and suburban locations and undisturbed natural areas thought to be 'pristine'.
- Pesticides used on crops have been found hundreds of miles downstream in drinking water that comes from rivers flowing through farmland

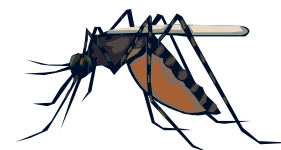


- **Non-discrimination**

- Improper use or application leads to the elimination of all arthropod species and severe consequences for other wildlife.
- Can contribute to the collapse of soil eco-systems by eliminating soil bacteria and funguses.

- **Resistance**

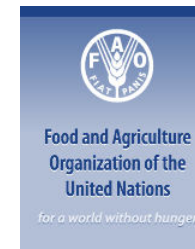
- Long term or improper use of insecticides can produce resistance in target species.
- In Sri Lanka, parts of India, Pakistan, Turkey and Central America, DDT resistance in mosquitoes has forced a shift to organophosphate and carbamate insecticides for malaria control.





International Organizations/Agreements concerned with pesticide problems

- **United Nations Food and Agriculture Organization (FAO)**
 - Founded in 1946.
 - Advises countries which import pesticides on how to manage them.
- **Stockholm Convention on Persistent Organic Pollutants**
 - Ratified by 134 nations; entered into force May 2001.
 - International agreement concerning Persistent Organic Pollutants (POPs), “chemical substances that persist in the environment, bio-accumulate through the food web, and pose a risk of causing adverse effects to human health and the environment”.
 - Bans or severely restricts the production, use, trade and disposal of 12 POP’s.
- **Rotterdam Convention**
 - Prior Informed Consent Procedure for Certain Hazardous Chemicals and Pesticides in International Trade (PIC Convention)
 - Ratified by 11 nations; entered into force February 2004.
 - Nations must know about imports of chemicals that are banned or severely restricted in the exporting country, or are severely hazardous pesticide formulations.
- **Aarhus Protocol on Persistent Organic Pollutants**
 - Amendment to the 1979 Geneva Convention on Long Range Trans-boundary Air Pollution.
 - Deals with Long Range Transport caused by the semi-volatile and persistent nature of these chemicals combined with global wind distribution.





Current Status

- Large stockpiles of obsolete pesticides are located in many developing countries.
- Many are beyond the manufacturers expiration date.
- Stocks are not inventoried or secured.
- Materials are routinely used by untrained applicators resulting in
 - over application
 - personal exposure
 - contamination of fields, farms, storage facilities and other people.
- <http://www.fao.org/ag/AGP/AGPP/Pesticid/p.htm> has useful information on Pesticide management.





Pesticide management issues: Global

- Large stockpiles of pesticides exist as a result of:
 - Changes in agricultural/environmental policies in developed nations
 - Ratification of several international treaties and conventions.
 - These pesticides considered ‘obsolete’ by the FAO.
- Many pesticides transferred to the developing world
 - Demand exists throughout the developing world
 - Especially DDT to combat malaria.
 - International manufacturers continue production
 - Large amounts of recently banned pesticide products from Europe and North America were freely given to any nation that asked for them.





Pesticide management issues: Local

- **Usage**

- Pesticides all come with specific instructions for application.
- Individuals applying these pesticides should be:
 - Well trained
 - Familiar with the inherent hazards posed by these chemicals.
 - Knowledgeable about regional soil conditions and pest organisms.

- **Application**

- Bulk quantities can lack chemical property data and manufacturers instructions on utilization, application and precautions.
- Some pesticide “systems” require the use of special emulsifiers for proper usage.
- Excessive application due to lack of proper instructions occurs frequently.
- Over-application is leading cause of human illness and water/soil contamination/degradation.





Pesticide management issues: Local

- **Storage**

- **Obsolete stocks of pesticides are found in long term storage, outdoors, exposed to the elements.**
- **Intense sunlight, heat, humidity and precipitation lead to loss of potency.**
- **Chemical weathering can produce toxic by-products.**
- **Damaged containers lead to distribution by wind, storm run-off, theft and vandalism.**
- **Obliterated labels lead to improper application and usage.**
- **Stock piles should be stored out of direct sunlight or precipitation and under lock and key.**



Pesticide management issues: Local

- **Disposal**

- Proper disposal is time consuming and expensive.
- Very few countries can properly dispose of these chemicals.
- Until funding/infrastructure allow for proper local/regional disposal, provide physical protection for and limit access to these materials.
- Improperly disposed of pesticides can:
 - Cause innocent people to become sick or to die from inadvertent exposure.
 - Can also cause livestock to become sick or to die.
 - Can make them easy to steal for criminal/ terrorism uses.



Obsolete Pesticide Recommendations

- **Inventory**
 - Many countries do not have central inventory sources
 - Makes it difficult to address the problem of disposal
 - Makes it easier for terrorists to steal pesticides
 - What do you have in your country?
 - Who knows the answers?
 - Is it usable or deteriorated?
 - Do you really need it? Will you really use it?
- **Usable**
 - Make safe/secure
 - Repackage/re-label if necessary
 - Store securely until use by trained personnel
- **Not usable**
 - Make safe/secure
 - Repackage/re-label if necessary
 - Store securely until proper disposal



Chemical Dual-use Awareness and International Chemical Controls

Nancy B. Jackson, PhD

International Chemical Threat Reduction Department
Sandia National Laboratories



Chemical dual-use awareness

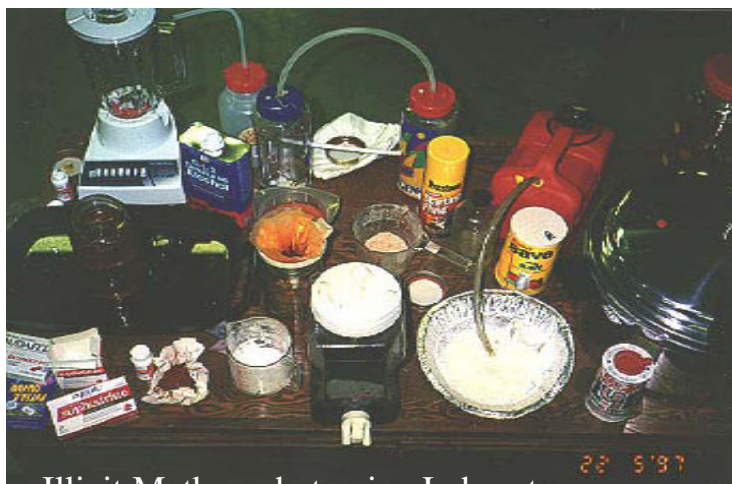
Dual use chemicals: Chemicals used in industry or everyday life that can also be used in bad ways.





Dual-use chemical example: Pseudoephedrine

- Pseudoephedrine is a common ingredient in cold medicines
- Precursor to crystal methamphetamine
- Recipes for conversion available on web



- Clandestine meth labs in US during 2002
 - Caused 194 fires, 117 explosions, and 22 deaths
 - Cost \$23.8 million for cleanup
 - Dumped chemicals led to
 - deaths of livestock
 - contaminated streams
 - large areas of dead trees and vegetation



Dual-use chemical example: Cyanide



Therence Koh/AFP/Getty Images



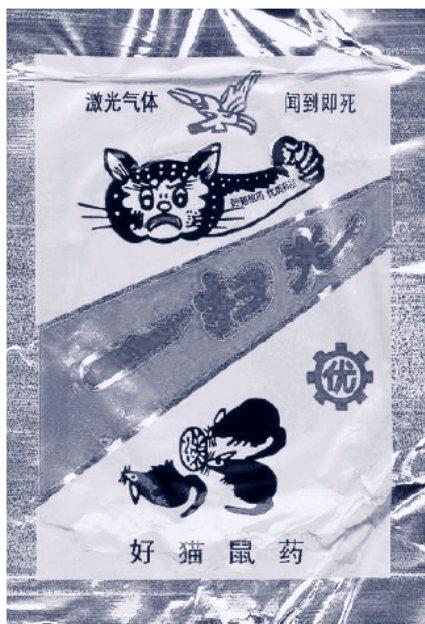
- Widely used in mining and metal plating industries, but is also a well known poison.
- Product tampering*
 - Tylenol capsules
 - laced with KCN
 - 7 deaths, fall 1982, Chicago, Illinois, USA
 - Led to tamper-proof product packaging
- Popular with criminals and terrorists because it is relatively easy to obtain
- HCN is CW agent AC



Dual-use chemical example: Pesticides

- Widely used in homes and agriculture, but also used to poison people.

FIGURE. Package of Chinese rodenticide implicated in the poisoning of a female infant aged 15 months — New York City, 2002



Photo/New York City Poison Control Center

- Dushuqiang (Strong Rat Poison)
 - Outlawed in China in the mid-1980s, but was still available
 - Nanjing, China, Sept. 2002
 - 38 people killed by poison in snack-shop food, >300 sick
 - Jealously by rival shop owner
 - Hunan, China, Sept. 2003
 - 241 people poisoned by cakes served by school cafeteria
 - Motive and perpetrator unknown
 - Tongchuan City, Shaanxi, China, April 2004
 - 74 people poisoned by scallion pancakes
 - Motive and perpetrator unknown
 - 5 other incidents reported between 1991 and 2004

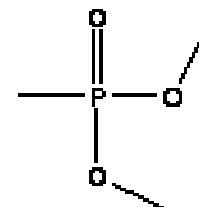
Ann. Emerg. Med., Vol. 45, pg. 609, June 2005



Many lab/industrial chemicals have dual uses

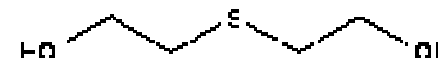
- **Dimethyl methyl phosphonate (DMMP)**

- Flame retardant for:
 - building materials, furnishings, transportation equipment, electrical industry, upholstery
- Nerve agent precursor



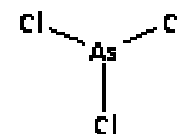
- **Thiodiglycol**

- Dye carrier, ink solvent, lubricant, cosmetics, anti-arthritic drugs, plastics, stabilizers, antioxidants, photographic, copying, antistatic agent, epoxides, coatings, metal plating
- Mustard gas precursor



- **Arsenic Trichloride**

- Catalyst in CFC manufacture, semiconductor precursor, intermediate for pharmaceuticals, insecticides
- Lewisite precursor

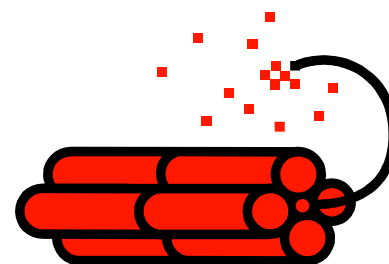


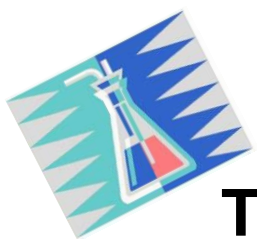
From: Chemical Weapons Convention: Implementation Assistance Programme Manual (on CD)



Dual-use Chemicals: Explosives

- Theft of conventional explosives
 - Chemical suppliers
 - Users such as mines or construction sites
- Diversion of industrial or laboratory chemicals
 - Chemical suppliers
 - Chemical factories
 - Academic teaching or research laboratories
 - Disposal sites





Theft / manufacture of explosives: Fertilizer Bomb



Photo: US DOD

- Ammonium nitrate fertilizer and fuel oil (diesel, kerosene)
- Used to bomb Alfred P. Murrah building in Oklahoma City, OK, USA
 - with nitromethane and commercial explosives
 - 168 dead, including children
 - April 1995
- Favored by IRA, FARC, ETA, etc.



Diversion of industrial / laboratory chemicals: Sodium azide



- **Widely available from older automobile airbags**
 - 1980s to 1990s
- **Poisonous**
- **Reacts explosively with metals**
 - Biological laboratory drains have exploded from discarded waste solutions containing NaN_3 as a preservative.
- **Has been found in possession of terrorists**



Diversion of industrial / laboratory chemicals

- Malaysian police arrested 36-year-old Alias Osman on June 9, 2003 in a Kuala Lumpur suburb. They claim he was a member of the militant Islamic group Jemaah Islamiah (JI). Police say he led them to an oil-palm plantation where a cache of chemicals was buried, including an unspecified amount of sodium azide. Most of the chemicals seized, potassium chloride*, calcium chloride* and aluminum powder, were similar to those used in the Bali bomb blasts.**

* Should be chlorate, not chloride

** Different devices may have used different explosive mixtures. Analysis gave evidence for chlorate and TNT

Simon Elegant, "Poisonous Minds," Time (Asia) 161, June 30, 2003.

<http://www.time.com/time/magazine/article/0,9171,501030630-460248,00.html>, viewed Nov. 2007

D. Royds, S.W. Lewis, A.M. Taylor, Talanta 67 (2005) 262–268



Diversion of industrial / laboratory chemicals: Quote from the “Terrorists Handbook”

2.1 ACQUIRING CHEMICALS

The first section deals with getting chemicals legally. This section deals with "procuring" them. The best place to steal chemicals is a college. Many state schools have all of their chemicals out on the shelves in the labs, and more in their chemical stockrooms. Evening is the best time to enter lab buildings, as there are the least number of people in the buildings, and most of the labs will still be unlocked. One simply takes a bookbag, wears a dress shirt and jeans, and tries to resemble a college freshman. If anyone asks what such a person is doing, the thief can simply say that he is looking for the polymer chemistry lab, or some other chemistry-related department other than the one they are in.

9.0 CHECKLIST FOR RAIDS ON LABS

http://www.totse.com/en/bad_ideas/irresponsible_activities/168593.html, downloaded Nov. 2007



International chemical control groups



ORGANISATION FOR THE PROHIBITION OF CHEMICAL WEAPONS

Chemical weapons convention

The Australia Group

Export controls

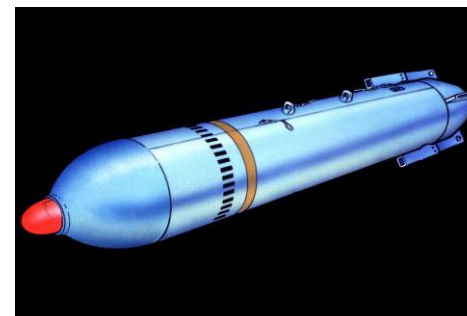
UN Security Council Resolution 1540



Organization for the prohibition of chemical weapons (OPCW)



- International group headquartered in The Hague, Netherlands
 - <https://www.opcw.org/index.html>
- Chemical weapons convention (CWC)
 - International treaty which bans the development, production, stockpiling, transfer and use of chemical weapons
- Promotes international cooperation in peaceful uses of chemistry
- Protecting each other





Chemical Weapons Convention (CWC)

- **International treaty which bans the development, production, stockpiling, transfer and use of chemical weapons**
 - **Entered into force in April 1997 with 87 State Parties participating**
 - **Today: 183 nations have joined, 5 others have signed, only 7 have not taken any action.**
 - **Each nation enacts appropriate laws**
 - **Each nation agrees to assist other Member States**





CWC: Destroy existing stockpiles and facilities

- **Twelve States parties have declared CW production facilities.**
 - **Bosnia and Herzegovina**
 - **China**
 - **France**
 - **India**
 - **Islamic Republic of Iran**
 - **Japan**
 - **Libyan Arab Jamahiriya**
 - **Russian Federation**
 - **Serbia**
 - **United Kingdom of Great Britain and Northern Ireland**
 - **United States of America**
 - **another State Party**
- **As of August 2007, 42 of 65 declared CW production facilities have been certified as destroyed, 19 converted to peaceful purposes.**
- **As of August 2007, 23,912 metric tonnes of CW agent has been destroyed out of 71,330 metric tonnes declared.**
- **On 11 July 2007, the OPCW confirmed the destruction of the entire chemical weapons stockpile in Albania.**
- **Includes old and abandoned CW munitions**



CWC: Prevent spread or production of new chemical weapons



- States declare and agree to inspections of many other chemical facilities, depending on chemical type and amount produced
- Over 3,000 inspections have taken place at 200 chemical weapon-related and over 850 industrial sites on the territory of 79 States Parties since April 1997
- Worldwide, over 5,000 industrial facilities are liable to inspection





CWC: Chemicals on schedules subject to verification measures



- **Schedule 1:**
 - Known CW agents
 - Highly toxic, closely related chemicals, or CWA precursors
 - Has little or no peaceful application
- **Schedule 2:**
 - Toxic enough to be used as a CWA
 - Precursor to or important for making a Schedule 1 chemical
 - Not made in large commercial quantities for peaceful purposes
- **Schedule 3:**
 - Has been used as a CWA
 - Precursor to, or important for making a Schedule 1 or 2 chemical
 - Is made in large commercial quantities for peaceful purposes
- **Unscheduled Discrete Organic Chemicals (UDOC)**
- **Lists of scheduled chemicals follow: also in documents on CD**





CWC: Reporting requirements

- **Use/transfer of these chemicals is allowed for research, medical, or pharmaceutical purposes.**
- **Reporting requirements depend on facility type, chemical types and amounts.**
 - **“Other Facility” type, as defined in CWC documents, most relevant here**
 - **Amounts of chemicals that would require that your National Authority approve the work and report your institution annually to the OPCW**
 - **Schedule 1: 100 g aggregate**
 - **Schedule 2: 1 kg for 2A*, 100 kg for other 2A, 1 Tonne of 2B**
 - **Schedule 3: 30 Tonnes**
 - **UDOC: 30 or 200 Tonnes (lower number if contains P, S, or F)**

Caution:

Your country might require reporting of lower amounts!



Schedule 1 Chemicals

A. Toxic chemicals

- (1) O-Alkyl (<C10, incl. cycloalkyl) alkyl (Me, Et, n-Pr or i-Pr)-phosphonofluoridates, e.g.
 - Sarin: O-Isopropyl methylphosphonofluoridate
 - Soman: O-Pinacolyl ethylphosphonofluoridate
- (2) O-Alkyl (<C10, incl. cycloalkyl) N,N-dialkyl (Me, Et, n-Pr or i-Pr) phosphoramidocyanidates, e.g. Tabun: O-Ethyl N,N-dimethyl phosphoramidocyanidate
- (3) O-Alkyl (H or <C10, incl. cycloalkyl) S-2-dialkyl (Me, Et, n-Pr or i-Pr)-aminoethyl alkyl (Me, Et, n-Pr or i-Pr) phosphonothiolates and corresponding alkylated or protonated salts, e.g. VX: O-Ethyl S-2-diisopropylaminoethyl methyl phosphonothiolate
- (4) Sulfur mustards:
 - 2-Chloroethylchloromethylsulfide
 - Mustard gas: Bis(2-chloroethyl)sulfide
 - Bis(2-chloroethylthio)methane
 - Sesquimustard: 1,2-Bis(2-chloroethylthio)ethane
 - 1,3-Bis(2-chloroethylthio)-n-propane
 - 1,4-Bis(2-chloroethylthio)-n-butane
 - 1,5-Bis(2-chloroethylthio)-n-pentane
 - Bis(2-chloroethylthiomethyl)ether
 - O-Mustard: Bis(2-chloroethylthioethyl)ether

- (5) Lewisites:
 - Lewisite 1: 2-Chlorovinylchloroarsine
 - Lewisite 2: Bis(2-chlorovinyl)chloroarsine
 - Lewisite 3: Tris(2-chlorovinyl)arsine
- (6) Nitrogen mustards:
 - HN1: Bis(2-chloroethyl)ethylamine
 - HN2: Bis(2-chloroethyl)methylamine
 - HN3: Tris(2-chloroethyl)amine
- (7) Saxitoxin
- (8) Ricin

B. Precursors

- (9) Alkyl (Me, Et, n-Pr or i-Pr) phosphonyldifluorides, e.g. DF: Methylphosphonyldifluoride
- (10) O-Alkyl (H or <C10, incl. cycloalkyl) O-2-dialkyl (Me, Et, n-Pr or i-Pr)-aminoethyl alkyl (Me, Et, n-Pr or i-Pr) phosphonites and corresponding alkylated or protonated salts e.g. QL: O-Ethyl O-2-diisopropylaminoethyl methylphosphonite
- (11) Chlorosarin: O-Isopropyl methylphosphonochloridate
- (12) Chlorosoman: O-Pinacolyl methylphosphonochloridate





Schedule 2 Chemicals

A. Toxic chemicals

- (1) Amiton: O,O-Diethyl S-[2-(diethylamino)ethyl] phosphorothiolate and corresponding alkylated or protonated salts
- (2) PFIB: 1,1,3,3,3-Pentafluoro-2-(trifluoromethyl)-1-propene
- (3) BZ: 3-Quinuclidinyl benzilate

B. Precursors

- (4) Chemicals, except for those listed in Schedule 1, containing a phosphorus atom to which is bonded one methyl, ethyl or propyl (normal or iso) group but not further carbon atoms, e.g.
 - ethylphosphonyl dichloride
 - dimethyl methylphosphonate
 - Exemption: Fonofos: O-Ethyl S-phenyl ethylphosphonothiolothionate
- (5) N,N-Dialkyl (Me, Et, n-Pr or i-Pr) phosphoramidic dihalides
- (6) Dialkyl (Me, Et, n-Pr or i-Pr) N,N-dialkyl (Me, Et, n-Pr or i-Pr)-phosphoramidates

- (7) Arsenic trichloride
- (8) 2,2-Diphenyl-2-hydroxyacetic acid
- (9) Quinuclidin-3-ol
- (10) N,N-Dialkyl (Me, Et, n-Pr or i-Pr) aminoethyl-2-chlorides and corresponding protonated salts
- (11) N,N-Dialkyl (Me, Et, n-Pr or i-Pr) aminoethane-2-ols and corresponding protonated salts
 - Exemptions: N,N-Dimethylaminoethanol and corresponding protonated salts
 - N,N-Diethylaminoethanol and corresponding protonated salts
- (12) N,N-Dialkyl (Me, Et, n-Pr or i-Pr) aminoethane-2-thiols and corresponding protonated salts
- (13) Thiodiglycol: Bis(2-hydroxyethyl)sulfide
- (14) Pinacolyl alcohol: 3,3-Dimethylbutan-2-ol





Schedule 3 Chemicals

A. Toxic chemicals

- (1) Phosgene: Carbonyl dichloride
- (2) Cyanogen chloride
- (3) Hydrogen cyanide
- (4) Chloropicrin: Trichloronitromethane

B. Precursors

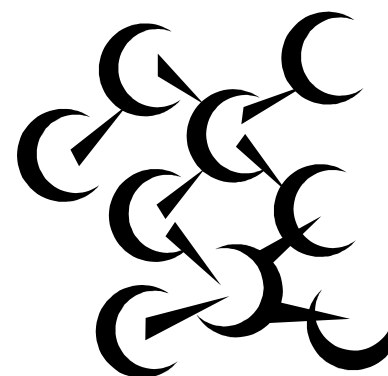
- (5) Phosphorus oxychloride
- (6) Phosphorus trichloride
- (7) Phosphorus pentachloride
- (8) Trimethyl phosphite
- (9) Triethyl phosphite
- (10) Dimethyl phosphite
- (11) Diethyl phosphite
- (12) Sulfur monochloride
- (13) Sulfur dichloride
- (14) Thionyl chloride
- (15) Ethyldiethanolamine
- (16) Methyldiethanolamine
- (17) Triethanolamine





Unscheduled discrete organic chemicals (UDOC)

- Also subject to CWC reporting, but only for large amounts.
- "Discrete Organic Chemical" means any chemical belonging to the class of chemical compounds consisting of all compounds of carbon except for its oxides, sulfides and metal carbonates, identifiable by chemical name, by structural formula, if known, and by Chemical Abstracts Service registry number, if assigned.



From CWC text – on CD



OPCW: Promotes international cooperation in peaceful uses of chemistry



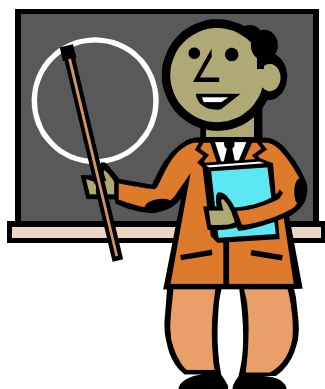
- Associates program
- Analytical skills development course
- Conference support program
- Research projects program
- Internship Support Program
- Laboratory Assistance Program
- Equipment Exchange Program





OPCW: Protecting each other

- Each member state can request assistance from other member states in the event of a threat or attack, including chemical terrorism
- This can take the form of expertise, training, materials, and/or equipment





Australia Group

- **An informal arrangement to minimize the risk of assisting chemical and biological weapon (CBW) proliferation.**
 - **Harmonising participating countries' national export licensing measures**
 - **Started in 1985 when Iraq CW program was found to have diverted chemicals and equipment from legitimate trade**
- **40 nations plus European Commission participate**



Australia Group: Export Controls

- **Controls exports of:**
 - **63+ Chemical weapon agent precursor chemicals**
 - **Dual-use chemical manufacturing facilities and equipment and related technology**
 - **Dual-use biological equipment and related technology**
 - **Biological agents**
 - **Plant pathogens**
 - **Animal pathogens**
- **Includes no-undercut policy**
 - **Countries won't approve an export that another member country denied**





UN Security Council Resolution 1540

- **Unanimously passed on 28 April 2004**
- **Member States:**
 - **must refrain from supporting non-State actors in developing, acquiring, manufacturing, possessing, transporting, transferring or using nuclear, chemical or biological weapons and their delivery systems.**
 - **must establish domestic controls to prevent the proliferation of nuclear, chemical and biological weapons, and their means of delivery, including by establishing appropriate controls over related materials.**
- **Enhanced international cooperation on such efforts is encouraged, in accord with and promoting universal adherence to existing international non-proliferation treaties.**



Basics of Systematic, Risk-based Approaches to Facility Security

Nancy B. Jackson, PhD

International Chemical Threat Reduction Department
Sandia National Laboratories



Facility Security Helps Avoid Undesirable Consequences

- **Death/Severe Injury**
- **Chemical contamination**
 - People
 - Environment
- **Political Instability**
- **Economic Loss**
- **Industrial capacity loss**
- **Negative public psychological effect**
- **Adverse media coverage**





Many kinds of chemical facilities need to be secured

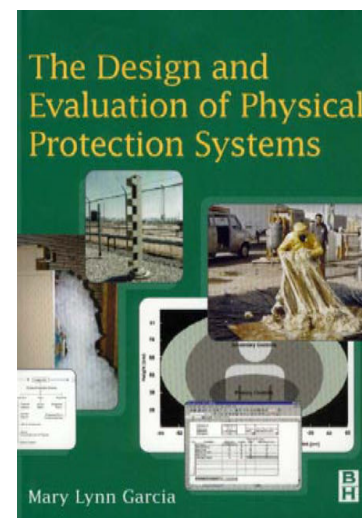


- **Small-scale research laboratories**
 - Many different chemicals used in small amounts
- **Large-scale manufacturing plants**
 - Limited types of chemicals used in large amounts
- **Security measures need to match facility and threat**
 - Can't afford to defend against all imaginable threats



Systematic approaches to facility security

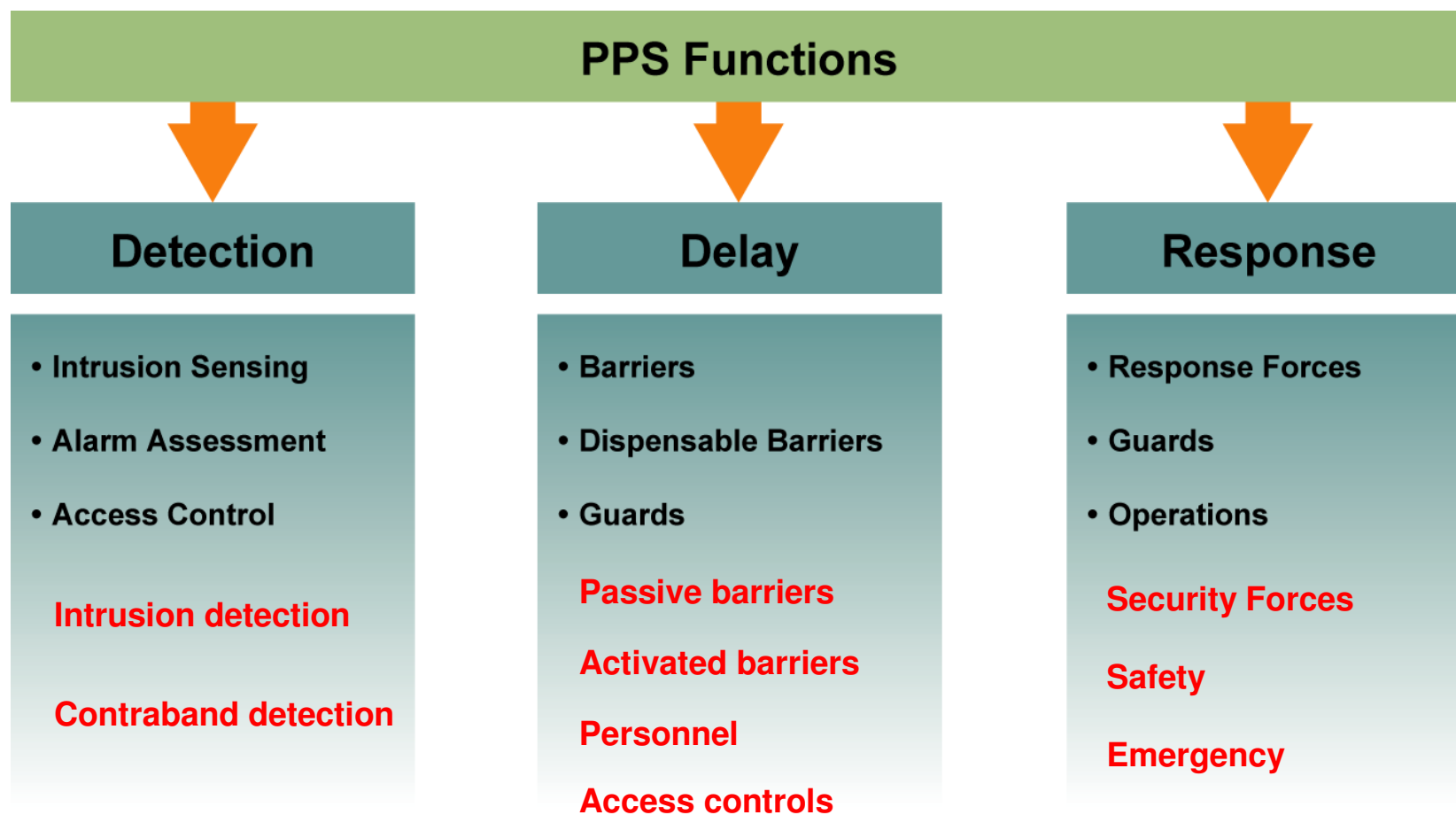
- **Balance risks**
- **Systematically decide what operational practices or equipment purchases will be most effective**
- **Originally developed for designing physical security systems for high-value items**
 - **Nuclear facilities**
- **Methodology applied to other high-value facilities**
 - **Large chemical plants**
 - **Electric power plants and transmission lines**
 - **Water treatment plants**



<http://www.sandia.gov/ram/>



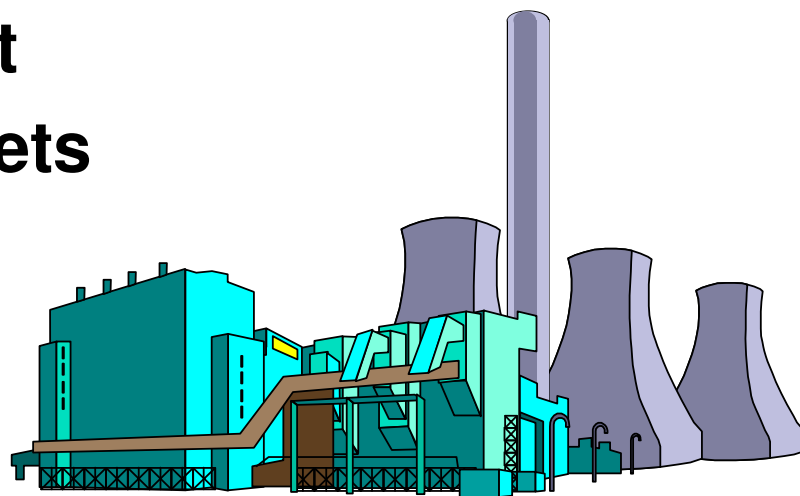
What should a Protection *SYSTEM* do?





Protection System Design Objectives

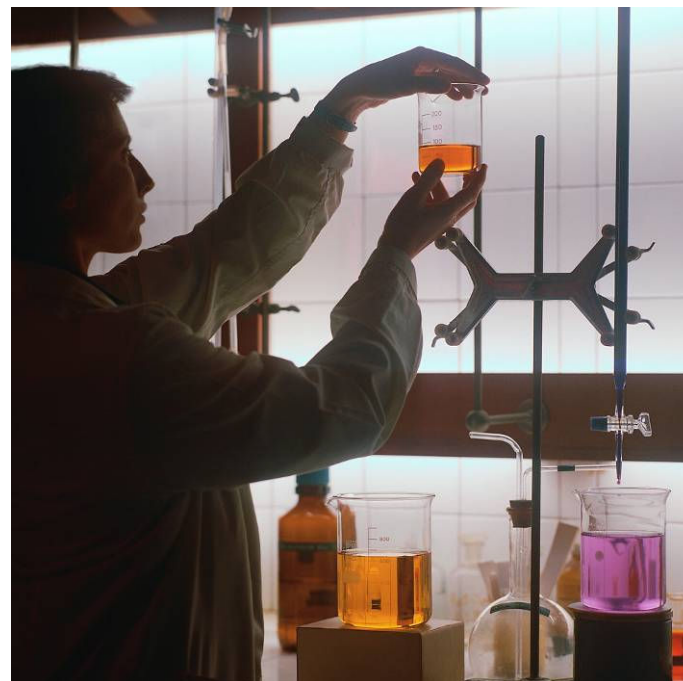
- **Understand what to protect and from whom:**
 - **Characterize the facility**
 - **Define the threat**
 - **Identify the targets**





Facility Characterization

- **Characterize the facility considering:**
 - **Mission**
 - **Operations**
 - **Budget**
 - **Safety**
 - **Legal Issues**
 - **Regulatory Issues**





Facility Characterization

- **Characterize the facility in terms of**
 - Site boundary
 - Buildings (construction and HVAC systems)
 - Room locations
 - Access points
 - Processes within the facility
 - Existing Protection Systems
 - Operating conditions (working hours, off-hours, potential emergencies)
 - Safety considerations
 - Types and numbers of employees
 - Legal and regulatory issues



Facility Characterization

- **Facility characterization provides important data that will:**
 - **Help identify locations and assets to be protected**
 - **Provide important details about the facility that will allow system designers to make design selections**
 - **Establish what existing Protection System components are already present at the facility**
 - **Document facility layout for use in analysis**



Design Basis Threat

- **Design Basis Threat (DBT) is the attributes and characteristics of potential adversaries, who might attempt unauthorized removal of sensitive material or sabotage, against which a physical protection system is designed and evaluated.**
- **At the national level, the DBT is typically defined by the government.**
- **At the facility level, also:**
 - **Consider local threats**
 - **Local criminals, terrorists, protestors**
 - **Consider insider threats**
 - **Employees and others with access**



Threat Definition

- **Using all information sources determine:**

Classes of adversaries

Outsiders—no authorized access

Insiders—authorized access

Collusion—between Outsiders and Insiders





What Might Motivate Adversaries?

- **Terrorists**

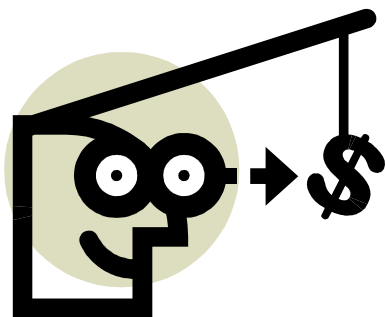
- Ideology

- **Criminals**

- Financial

- **Activists**

- Ideology



- **Insiders**

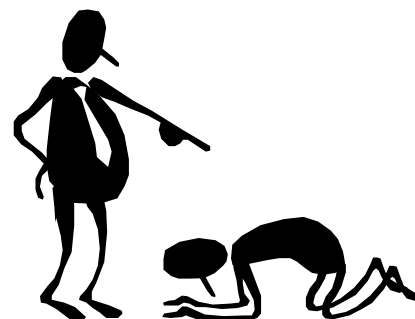
- Ego

- Ideology

- Revenge

- Financial

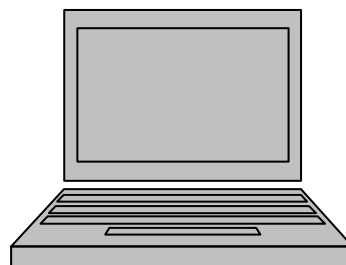
- Coercion





Target Identification

- **Determine the possible targets for the following actions:**
 - **Sabotage**
 - Identify vital areas to protect
 - **Theft of material or information**
 - Identify location of material to protect





Systems are designed to protect specific targets against specific threats

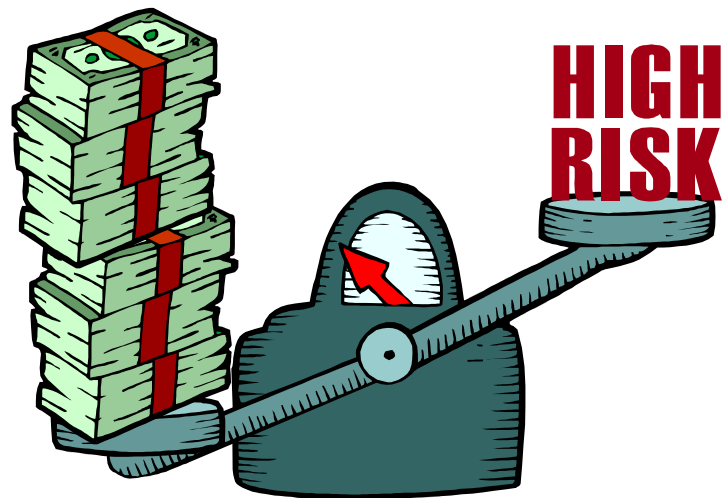
- **Targets**
 - Facility targets exist
 - Undesirable theft or sabotage consequences
- **Threats**
 - National / International level threats
 - Local threats

Consequences + Threats = Need for protection



The Main Question

- How much risk is acceptable versus the cost of reducing that risk?
- Must manage multiple risks in a holistic manner
 - Financial
 - Liability
 - Health and safety
 - Business/mission
 - Security





Concept of Risk

- Risk associated with adversary attack is a function of:
 - Severity of consequences of an event
 - Likelihood of adversary attack
 - Likelihood of adversary success in causing an undesired event
- Risk is a relative ranking not an absolute number
- Combines three relevant factors into a single parameter
- Allows comparisons of threat, security system, and consequence variations
- Helps in prioritizing/justifying requirements and budgeting (efficient allocation of resources)



Risk, Risk Assessment, and Vulnerability Assessment

- **Risk – *Measure*** of the potential damage to, or loss of, an asset based on the probability of an undesired event
- **Risk Assessment – *Process*** of analyzing threats to, and vulnerability of, a facility; determining the potential for losses; and identifying cost-effective corrective measures
- **Vulnerability Assessment – *Process*** in which qualitative/quantitative techniques are applied to detect vulnerabilities and to arrive at an effectiveness level for a security system



Risk Management

- **Risk mitigation usually includes a combination of:**
 - **Avoidance**
 - **Reduction**
 - **Spreading**
 - **Transfer**
 - **Acceptance**
- **Depend on specific facility and location**



Quantify Security Risk

- Three components:
 - Likelihood of attack (P_A)
 - Likelihood the Protection System will NOT stop the adversary ($1 - P_I \times P_N$), where
 - P_I = Probability of interrupting adversary
 - P_N = Probability of neutralizing adversary
 - Consequences of a successful attack (C)

$$\text{Risk} = P_A \times (1 - P_I \times P_N) \times C$$



Likelihood of Attack (P_A)

- Difficult to determine
- May be extremely low
- If worst case is assumed
 - $P_A = 1$ (assume there will be an attack)
 - Risk number is then “conditional” and risk equation becomes

$$\text{Risk} = (1 - P_I \times P_N) \times C$$



P_A Based On:

- Value of asset
- Usefulness to adversary
- Publicity value
- Availability
- Number of incidents at the installation or in the geographical area in the past
- Perceived regard for law enforcement
- Aggressor's perception of the possibility of success



Consequence (C)

- Quantifies the severity of occurrence of an event
- Number between 0 and 1
- If we assume protection is for the most critical assets, which might have a consequence value of 1.0, the risk equation becomes

$$\text{Risk} = (1 - P_I \times P_N)$$



Protective System Probabilities

- **Probability of interruption P_i**
 - The probability that the system will be able to detect and the response force interrupt the adversary
 - Computed as the cumulative detection probability along an adversary path
- **Probability of Neutralization P_N**
 - The probability that the Response Force will intercept, capture, or cause the adversary to flee



System Effectiveness

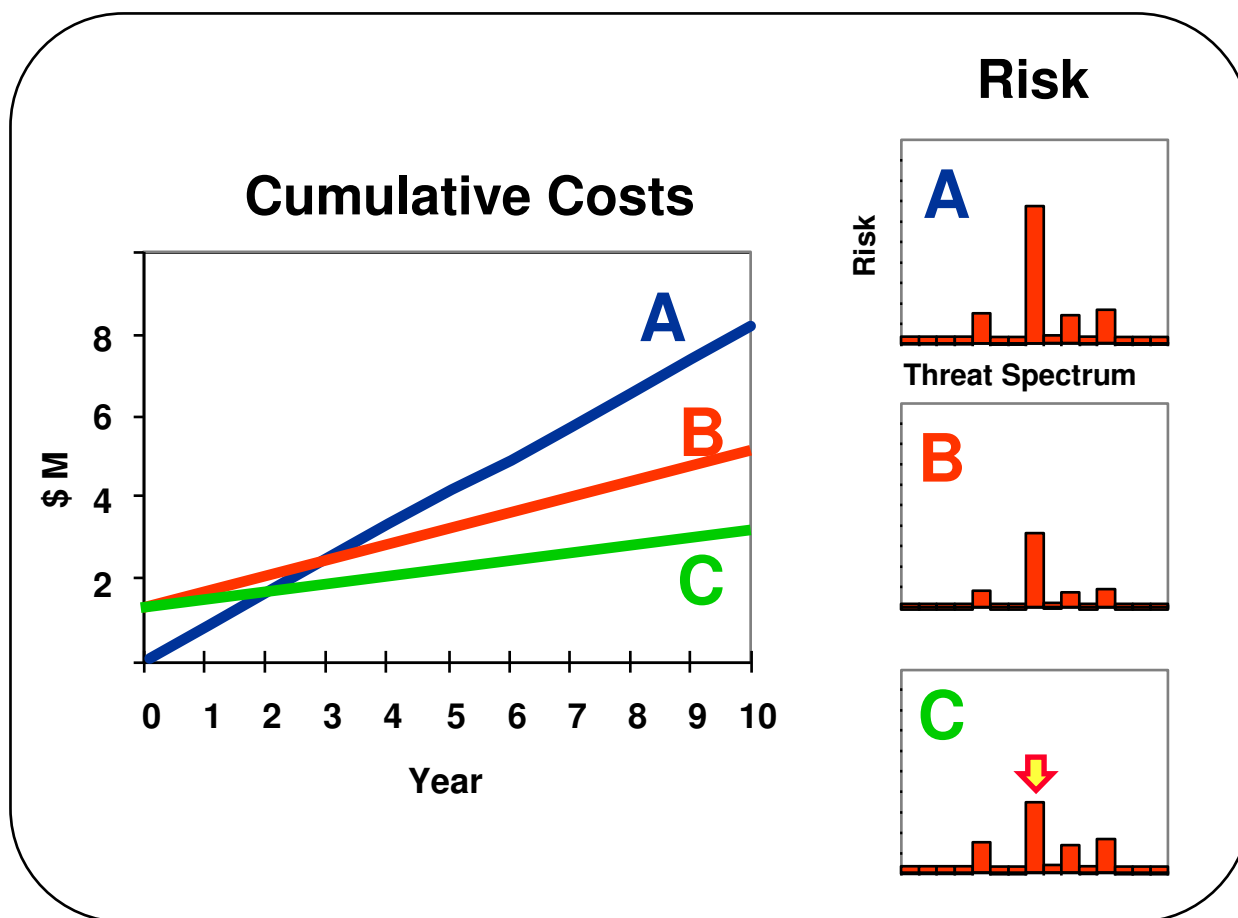
- Probability of Protection System effectiveness is $P_I \times P_N$
 - Derived from system modeling
 - A number between 0 and 1

$$\text{Risk} = (1 - P_I \times P_N)$$

- Residual risk after allowing for protection system effectiveness

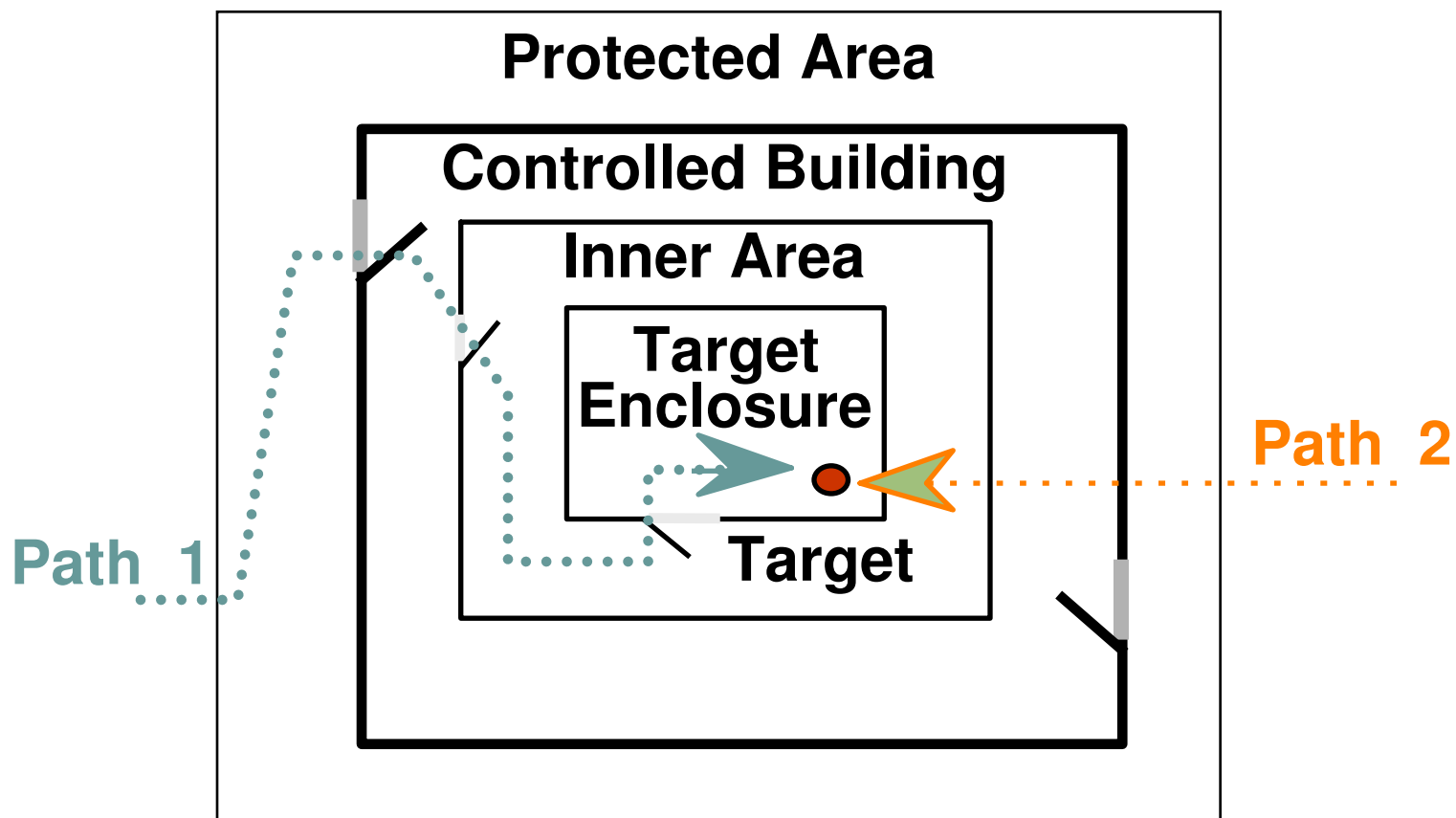


Cost Versus Risk



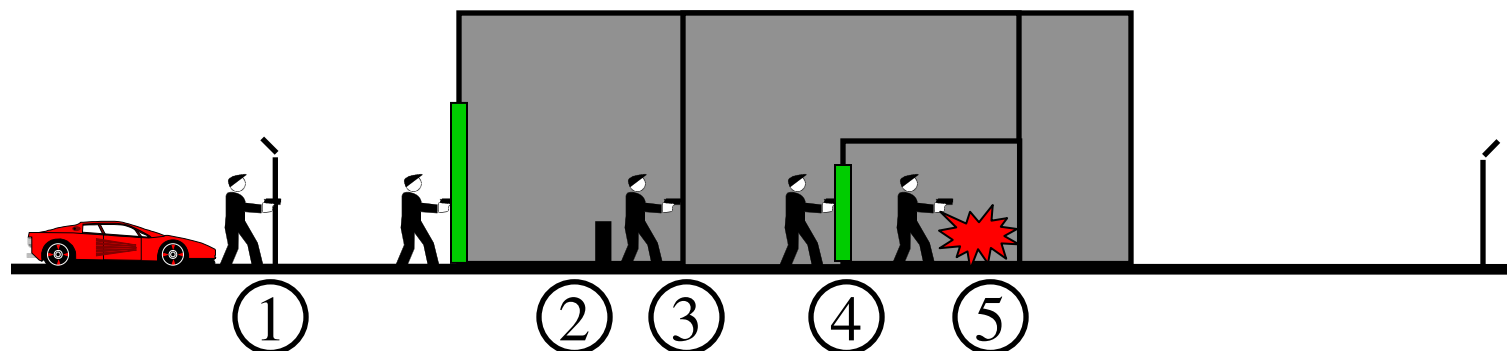


Multiple Adversary Paths to Target





Single Path Example

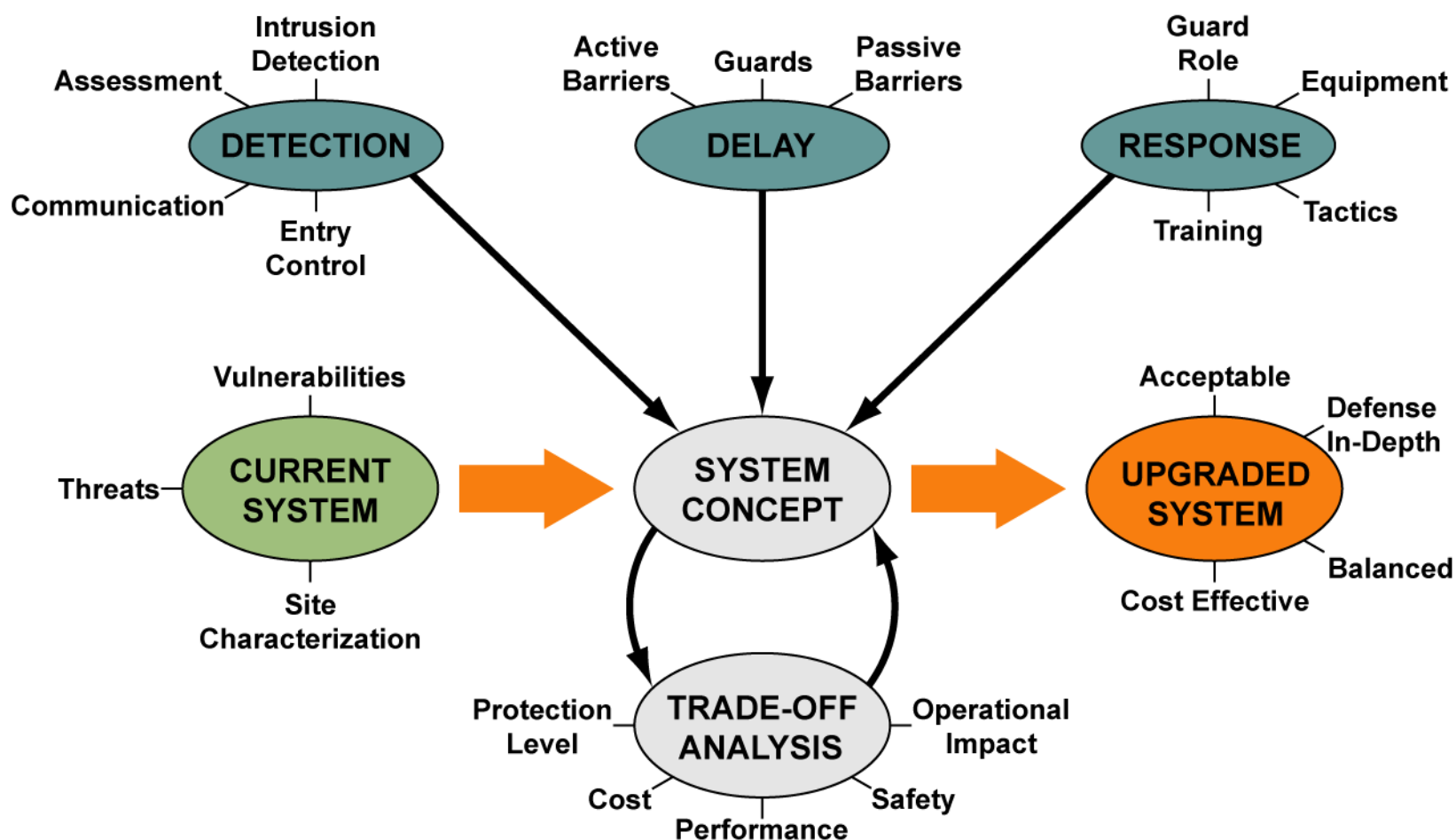


#. Action (Probability of Detection, Delay Time)

1. Penetrate fence (0.1, 10s)
2. Penetrate outer door (0.1, 15s)
3. Penetrate wall (0.5, 60s)
4. Penetrate inner door (0.1, 20s)
5. Sabotage target (0.9, 300s)



System Integration





Components of Chemical Security and Relationships Between Chemical Safety and Security

Nancy B. Jackson, PhD

International Chemical Threat Reduction Department
Sandia National Laboratories



Chemical Security

- Is your Department secure?
- How easy would it be for someone to steal chemicals?
- Are your chemistry stockrooms, classrooms and research labs always locked and secure?
- Is someone always there when these rooms are open?
- Do you check your orders when chemicals arrive to be sure some chemicals are not missing?





Components of Chemical Security

- Physical security of site
- Personnel management
- Information security
- Management of chemical security activities
- Allocation of chemical security responsibilities
- Development of emergency plans
- Chemical security training



Goal: Ensure that you don't accidentally help a criminal or a terrorist get dangerous chemicals



Chemical Security: Physical Site

LOCK UP!!



Controlled drugs

Chemical Surety Agents

Highly toxic chemicals





Chemical Security: Personnel Management

- Guard against both Insider and Outsider threat
- Does anyone check on people entering the building?
- Who has keys? How do they get authorized?
 - Building
 - Stockroom
 - Individual Labs
- When someone leaves, do you make sure they turn in keys?
- Don't want people making duplicate keys





Chemical Security: Information security

- **How do you track chemical inventory?**
 - Is the information secured so unauthorized people can't read it or alter it?
- **Would you know if:**
 - some toxic chemicals disappeared overnight?
 - some toxic chemicals didn't arrive?
 - someone was ordering chemicals in the name of your institution but diverting them?

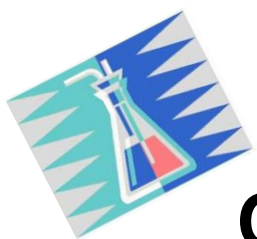




Chemical Security: Assign Responsibilities

- **Identify people who will be responsible for various chemical security activities**
 - Physical security and building modifications
 - Chemical tracking and reporting
 - Personnel and access management
 - Information management
 - Emergency planning
- **Ensure that they have the time and resources to do the job**
- **Integrate with chemical safety responsibilities**





Chemical Security: Professional behavior

- A Chemical Professional needs to use their scientific knowledge in a responsible manner



- A Chemical Educator needs to train their students to use their scientific knowledge in a responsible manner



Relationships between chemical safety and security

- **Chemical safety:** Protect against accidents
- **Chemical security:** Protect against deliberate harm
- Many practices are the same for chemical safety and security
- But there are a few areas of conflict





Good practices for both chemical safety and security

- **Minimize use of hazardous chemicals**
 - Replace with less-hazardous chemicals, if possible
 - Reduce scale of experiments
- **Minimize supply of hazardous chemicals on hand**
- **Restrict access to hazardous chemicals**
 - Know what you have
 - Know how to store, handle and dispose of what you have
 - Know who has access to materials, knowledge and expertise
- **Plan what to do in an emergency**



Conflicts between chemical safety and security: Information Sharing

Science generally means sharing information widely, but this may not always be advisable

- **Safety**

- Label everything so people can recognize hazardous chemicals.
- Alert community and especially emergency responders to possible chemical dangers.
- Share knowledge about chemical hazards so people know to be alert.

- **Security**

- Labels help identify targets for theft or attack.
- Sharing locations of chemicals can publicize targets for theft or attack.
- Sharing knowledge of chemical hazards could inspire harmful behavior (copy-cat criminals).



Conflicts between chemical safety and security: Facility exits

- Locking exit doors is secure, but not safe.
 - For **safety**, we want people to be able to leave the facility quickly and by many routes.
 - For **security**, we want to control exits as well as entrances so chemicals (or equipment) don't get taken.





Setting priorities

- Labs need to be **safe**, **secure** and **productive**
 - Policies and practices need to be flexible enough to allow for the uncertainties of research.
 - Policies and practices need to align with local laws, regulations, practices and culture. Can't just copy policies from somewhere else.
- Use risk-based security and safety measures.
 - Can't afford to defend against every imaginable hazard.
 - Identify threats, characterize facilities, identify alternatives, analyze costs vs. performance
- Be alert for suspicious activities or inquiries



Breakout Discussion: Next steps

- Break into smaller groups
- Discuss what you think should happen next
 - 30 minutes
- Report back action items to group





Summary

- **Chemical safety and security are important**
 - Academic chemistry laboratories are an attractive target for theft of chemicals
- **Chemical safety and security measures have a lot of overlap**
 - Attitudes and awareness
 - Policies
 - Physical additions/changes to buildings and labs





Workshop evaluation and feedback form

- Please help us improve this workshop by filling out and returning this form.

